

## Accepted Article

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# Gluing ionic liquids to oxide surfaces: Chemical anchoring of functionalized ionic liquids by vapor deposition onto cobalt(II) oxide

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**Abstract:** Ionic liquids (IL) hold a great potential as novel electrolytes for applications in electronic materials and energy technology. The functionality of ILs in these applications relies on their interface to semiconducting nanomaterials. Therefore, methods to control the chemistry and structure of this interface are the key to assemble new IL-based electronic and electrochemical materials. Here, we present a new method to prepare a chemically well-defined interface between an oxide and an IL film. An imidazolium-based IL, which is carrying an ester group, is deposited onto cobalt oxide surface by evaporation. The IL binds covalently to the surface by thermally activated cleavage of the ester group and formation of a bridging carboxylate. The anchoring reaction shows high structure sensitivity, which implies that the IL film can be “glued” selectively specific oxide surfaces.

Solar cells, fuel cells, batteries or flexible electronic devices, these are just a few of the many application fields in which ILs might be used as “designer electrolytes” in the near future.<sup>[1]</sup> The high application potential arises from the unique physical and chemical properties of ILs: ILs have an extremely low vapor pressure, which enables the preparation of non-volatile liquid coatings.<sup>[2]</sup> In electrochemical applications, many ILs show very high stability, i.e., large electrochemical windows.<sup>[1a,e]</sup> Along with this, their molecular structure is versatile, implying that the physicochemical properties of the IL (viscosity, density, gas solubility, miscibility, thermal stability) can be tailored to fit the specific application in mind.

With respect to the above mentioned applications in energy technology and electronics, the interface between the IL and the solid electrode is often the most critical building block of the device. This is because the functionality of many materials arises from transport of electrons, protons or chemical species across the solid/liquid interface.<sup>[1a,3]</sup> Despite its great importance, our understanding of such interfaces and our capabilities to engineer them at the microscopic level are quite limited. From the point of view of theory, the description of ILs as “non-classical” electrolytes is demanding and controversially disc-

ussed.<sup>[1a]</sup> From the point of view of analytics, solid/liquid interfaces are inherently a great challenge and, only recently, with the advent of “ionic liquid surface science” a better understanding is about to emerge.<sup>[4]</sup> And, finally, from the point of materials synthesis, recipes for preparing well-defined ionic liquid/solid interfaces are scarce, on the one hand because of our poor understanding of these systems, on the other hand because conventional preparation recipes cannot be easily transferred to IL-based materials.

Particularly challenging are IL/oxide interfaces, which play an important role in catalytic materials, solar cells, and organic electronic devices.<sup>[4a,5]</sup> The common method to immobilize ILs on oxides is by using silanol chemistry, but this method is limited to silicon-containing surfaces and, therefore, less suitable for applications in which the electronic properties of the oxide are critical.<sup>[6]</sup> In such applications, organic molecules are typically anchored covalently via specific linker groups, such as carboxylic acids, phosphonic acids or others.<sup>[7]</sup> Such anchors could also be introduced into ILs but, in general, they will severely affect the thermal and electrochemical stability of the IL as well as its physical and chemical properties.<sup>[8]</sup>

In this work, we present a new method for anchoring of ILs to oxide surfaces. Instead of using a free carboxylic acid, we use an IL which carries an ester group at the imidazolium cation. The ester bond is cleaved in a thermally activated reaction with the oxide surface. In contrast to the carboxylic acid, the ester-functionalized IL shows a high thermal stability, so that the IL can be evaporated to coat the oxide materials by vapor deposition. Moreover, we show for the specific case of cobalt oxides that the anchoring reaction is highly structure sensitive, i.e., the reactivity depends on the arrangement of Co cations at the surface.

Specifically, we applied infrared reflection absorption spectroscopy (IRAS) to follow the adsorption of 3-(4-isopropoxy-4-oxobutyl)-1-methylimidazolium bis(trifluoromethylsulfonyl)imide ([IPBMIM][NTf<sub>2</sub>]) (Scheme 1) on two atomically-defined cobalt oxide surfaces, Co<sub>3</sub>O<sub>4</sub>(111) and CoO(100). To deposit the IL onto the surfaces, we applied physical vapor deposition (PVD), a new and versatile method for the deposition of IL with high thermal stability. The isopropylester was chosen instead of the free acid because of its higher stability and volatility. We found that the IL functionalized by a carboxylic acid group decomposes upon evaporation, most likely because of strong hydrogen bonding. In contrast, the ester-functionalized IL can be evaporated without decomposition. Decomposition-free PVD of [IPBMIM][NTf<sub>2</sub>] was verified by comparing the IR spectrum of multilayers prepared by PVD with the ATR IR spectrum (see Figure S3 in the Supporting Information). The synthesis of the ultrapure [IPBMIM][NTf<sub>2</sub>] is also described in the Supporting Information.

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## COMMUNICATION

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All experiments were performed under ultrahigh vacuum (UHV) taking advantage of the extremely low vapor pressure of ILs.<sup>[4b,c]</sup> In a unique fashion, this surface science approach allows us to identify the interactions at the IL/oxide interface and, in particular, the chemical transformation upon anchoring. In previous studies, detailed insights could be obtained into the growth behavior and molecular orientation upon physisorption of ILs on atomically defined oxides.<sup>[9]</sup> Surface science studies on reactive oxides are still extremely scarce, however. One rare example is our previous XPS study of [HMIM][NTf<sub>2</sub>] (3-hexyl-1-methylimidazolium bis(trifluoromethylsulfonyl)imide) on CeO<sub>2</sub>(111), in which we showed that the acidic hydrogen at C<sub>2</sub> position of imidazolium cation can be abstracted, leading to formation of surface-anchored organic products.<sup>[10]</sup>

In this work, cobalt oxide was chosen as a model surface because of its wide range of applications, for instance, in the fields of catalysis<sup>[11]</sup>, electrocatalysis<sup>[12]</sup>, magnetic materials.<sup>[13]</sup> Atomically-defined Co<sub>3</sub>O<sub>4</sub>(111) and CoO(100) thin films were prepared on an Ir(100) single crystal following a procedure developed by Heinz and Hammer<sup>[14]</sup> (see Supporting Information). The atomic structure of the cobalt oxide surfaces (see Scheme 2) was previously established by STM and LEED I-V analysis.<sup>[15]</sup> Briefly, the Co<sub>3</sub>O<sub>4</sub>(111) surface is terminated by Co<sup>2+</sup> ions with a Co<sup>2+</sup>-Co<sup>2+</sup> distance of 5.7 Å. In contrast, the CoO(100) surface is terminated both by Co<sup>2+</sup> and O<sup>2-</sup> ions with a Co<sup>2+</sup>-Co<sup>2+</sup> distance of about 3.0 Å. Recently, we investigated the anchoring of organic molecules carrying carboxylic acid groups on these surfaces.<sup>[16]</sup> In the present study we demonstrate that similar anchoring reactions are possible for ILs as well, using new ILs with ester-functionalized cations.

In isothermal experiments, [IPBMIM][NTf<sub>2</sub>] was deposited onto the freshly prepared cobalt oxide, while IR spectra were taken in-situ during deposition. Selected IR spectra for deposition of [IPBMIM][NTf<sub>2</sub>] onto Co<sub>3</sub>O<sub>4</sub>(111) at 300 K and 400 K are shown in Figure 1c. At 300K, we observe the appearance of a broad band centered at 1680 cm<sup>-1</sup>. As deposition continues, the latter band saturates while a sharp peak arises at 1728 cm<sup>-1</sup> and grows until the end of deposition. These two features can be assigned to the C=O stretching mode of the ester group in the [IPBMIM]<sup>+</sup> cation. While the band at 1728 cm<sup>-1</sup> is characteristic for the free ester group, the second band at 1680 cm<sup>-1</sup> is strongly broadened and red-shifted by 50 cm<sup>-1</sup>. We attribute these changes to an interaction of the ester group with the Co<sup>2+</sup> ions of the oxide surface. Apparently, this interaction weakens the C=O bond but it is not strong enough to break the ester group. Thus, we propose that the carbonyl groups are adsorbed on top of the Co<sup>2+</sup> ions, as schematically represented in Figure 1b. The free ester peak at 1728 cm<sup>-1</sup> appears only in the multilayer region where there is no direct contact of the IL with the surface (Here we define the monolayer as the film thickness up to which the cations and anions interact with the surface. This interaction is monitored by the cation band at 1680 cm<sup>-1</sup> and the anion bands at 1140 and 1216 cm<sup>-1</sup>, see below. After saturation of the monolayer, the IL adsorbs in the multilayer, i.e. without direct contact with the oxide). The band at 1575 cm<sup>-1</sup> in the multilayer region can be assigned to a C=C/C=N stretching mode of the imidazolium ring polarized in the imidazolium plane. Based on the metal surface selection rule (MSSR) of IRAS<sup>[17]</sup> and the fact that this band is not seen at low IL coverage (Figure 1c), we conclude that the imidazolium ring initially adopts a flat-lying geometry. However, the band is observed in the IL multilayer where there is no preferential orientation. By temperature-programmed IRAS we determined a multilayer

desorption temperature of 380 K. Accordingly, no IL multilayer is observed upon IL deposition at 400 K (see Figure 1c). Still we observe the adsorption of an IL monolayer, suggesting stronger interaction of the first IL layer with surface. Similar to deposition at 300 K, the broadened C=O band indicates that the carbonyl group of the ester interacts with the surface Co<sup>2+</sup> ions, while the more intense band at 1575 cm<sup>-1</sup> suggests a more upright standing orientation of the imidazolium ring (Figure 1a) at 400 K as compared to the flat-lying orientation in the monolayer at 300 K.

As for the [NTf<sub>2</sub>]<sup>-</sup> anion, the most prominent peaks, centered at 1140, 1216 and 1360 cm<sup>-1</sup>, could be attributed to the  $\nu_{\text{SO}_2,\text{sym}}$ ,  $\nu_{\text{CF}_3,\text{asym}}$ , and  $\nu_{\text{SO}_2,\text{asym}}$  modes, respectively. These assignments are based on our previous IRAS and density functional theory studies of [BMIM][NTf<sub>2</sub>] (3-butyl-1-methylimidazolium bis(trifluoromethylsulfonyl)imide) on Al<sub>2</sub>O<sub>3</sub> where the [NTf<sub>2</sub>]<sup>-</sup> anion was found to adopt a cis-conformation and preferably interacts with the oxide via the SO<sub>2</sub> groups.<sup>[18]</sup> Specifically, the  $\nu_{\text{SO}_2,\text{sym}}$  band is blue shifted by 30 cm<sup>-1</sup> from 1110 cm<sup>-1</sup> to 1140 cm<sup>-1</sup> at low coverage, reflecting the interaction of SO<sub>2</sub> group with the surface. Further, the intensity ratio of the bands at 1140 cm<sup>-1</sup> and 1216 cm<sup>-1</sup> decreases from the monolayer to the multilayer region, indicating a preferred orientation in the monolayer in which the SO<sub>2</sub> groups face the Co<sub>3</sub>O<sub>4</sub>(111) surface (see Figure 1d). A similar adsorption geometry was previously found for [NTf<sub>2</sub>]<sup>-</sup> on Al<sub>2</sub>O<sub>3</sub>.<sup>[18]</sup>

In-situ IR spectra recorded during deposition of [IPBMIM][NTf<sub>2</sub>] on the CoO(100) surface are shown in Figure 2c. At 300 K, the spectra are quite similar to those observed on Co<sub>3</sub>O<sub>4</sub>(111). Again, a broad band at 1680 cm<sup>-1</sup> indicates that the ester group of the [IPBMIM][NTf<sub>2</sub>] interacts with surface via its carbonyl function. Also, the anion peaks have similar positions and show similar intensity ratio as those observed on Co<sub>3</sub>O<sub>4</sub>(111). Therefore, we conclude that at 300 K the interaction mechanism and orientation of [IPBMIM][NTf<sub>2</sub>] are similar on both surfaces (see Figure 2b).

The situation changes drastically, however, if the IL is deposited onto CoO(100) at 400 K. Similar as for Co<sub>3</sub>O<sub>4</sub>(111), no multilayer is formed. The spectra of the adsorbed monolayer, however, are completely different from those observed on Co<sub>3</sub>O<sub>4</sub>(111). A new peak appears at 1412 cm<sup>-1</sup> while no C=O band is observed at 1680 cm<sup>-1</sup>. The [NTf<sub>2</sub>]<sup>-</sup> bands are identical to the anion bands of the monolayer at 300 K indicating that intact [NTf<sub>2</sub>]<sup>-</sup> is present also at 400 K.

These changes suggest a chemical transformation of the ester group. In fact, the band at 1412 cm<sup>-1</sup> is characteristic for the symmetric OCO stretching mode  $\nu_{\text{OCO},\text{sym}}$  of a surface carboxylate. In general, such a surface carboxylate can bind in bridging, tilted or monodentate geometry. From the absence of the antisymmetric OCO stretching band  $\nu_{\text{OCO},\text{asym}}$  (expected around 1550 cm<sup>-1</sup>) we can conclude that in the present case a bridging carboxylate is formed. The reason is that only for a symmetrically adsorbed bridging carboxylate the  $\nu_{\text{OCO},\text{asym}}$  mode is polarized parallel to the surface and, therefore, forbidden by the MSSR. Note, that the peak position is also consistent with our previous studies of phthalic acid on CoO(100) where bridging carboxylates were formed as well.<sup>[16a]</sup> Thus, we propose that upon deposition at 400 K, the ester group of [IPBMIM][NTf<sub>2</sub>] is cleaved, leading to formation of a surface-anchored imidazolium carboxylate. Interestingly, the C=C/C=N band at 1575 cm<sup>-1</sup> is more prominent than for the [IPBMIM][NTf<sub>2</sub>] monolayer deposited at 300 K. This observation suggests that

the anchoring reaction forces the imidazolium ring into a more upright standing geometry (see Figure 2a).

The different bonding mechanism on  $\text{Co}_3\text{O}_4(111)$  and  $\text{CoO}(100)$  can be rationalized on the basis of the differences in the surface structure. The cleavage of the ester bond, catalyzed by Lewis acid and base sites on the oxide, is thermodynamically driven by bonding of the carboxylate to the surface. The stability of the surface carboxylate, however, depends strongly on the adsorption geometry. Typically, bridging carboxylates are most strongly anchored, whereas carboxylates in other adsorption geometry (chelating or monodentate) are more labile. On  $\text{CoO}(100)$ , the distance between the surface  $\text{Co}^{2+}$  ions is 3.0 Å, which allows forming a very stable bridging carboxylate (see Scheme 2 and 3). In sharp contrast, the much larger  $\text{Co}^{2+}$ - $\text{Co}^{2+}$  distance of 5.7 Å on  $\text{Co}_3\text{O}_4(111)$  prevents this adsorption geometry. Instead, the formation of monodentate or chelating carboxylate (involving one surface  $\text{Co}^{2+}$  only) would be possible, however, these geometries are strongly disfavored in terms of their adsorption energy.<sup>[19]</sup> In a comparative study on different cobalt oxide surfaces we recently confirmed these differences in stability.<sup>[16a]</sup> In consequence, we expect a much lower driving force for the scission of the ester bond on  $\text{Co}_3\text{O}_4(111)$ , which explains why the anchoring reaction is observed on the  $\text{CoO}(100)$  surface only. Further details of the reaction mechanism and kinetics are currently explored using complementary surface science experiments.

In summary, we present a new method to “glue” an ionic liquid film to an oxide surface by formation of chemically anchored layer of cations. We used the functionalized IL [IPBMIM][NTf<sub>2</sub>] which carries an ester group at the imidazolium cation. The IL was deposited onto atomically-defined  $\text{Co}_3\text{O}_4(111)$  and  $\text{CoO}(100)$  surfaces under ultraclean UHV conditions. We showed that the IL can be anchored to the oxide surface through cleavage of the ester bond and formation of a bridging surface carboxylate. This anchoring reaction is highly structure dependent: Whereas the carboxylate-anchored IL film is readily formed on  $\text{CoO}(100)$ , the reaction does not occur on  $\text{Co}_3\text{O}_4(111)$ , only weakly adsorbed ester groups are formed. These differences in reactivity are attributed to the different arrangement of  $\text{Co}^{2+}$  ions on the two surfaces. We believe that this new functionalization method can be straightforwardly applied to other oxide surfaces as well, helping to prepare IL/oxide interfaces with enhanced stability and improved transport properties in electronic and electrochemical applications.

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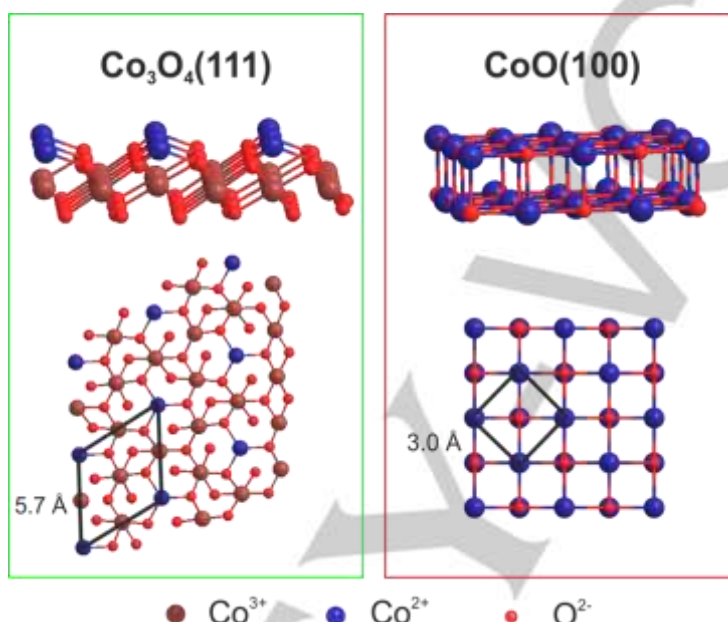
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**Keywords:** ionic liquid • ester functionalization • cobalt oxide • chemical anchoring • vapour deposition

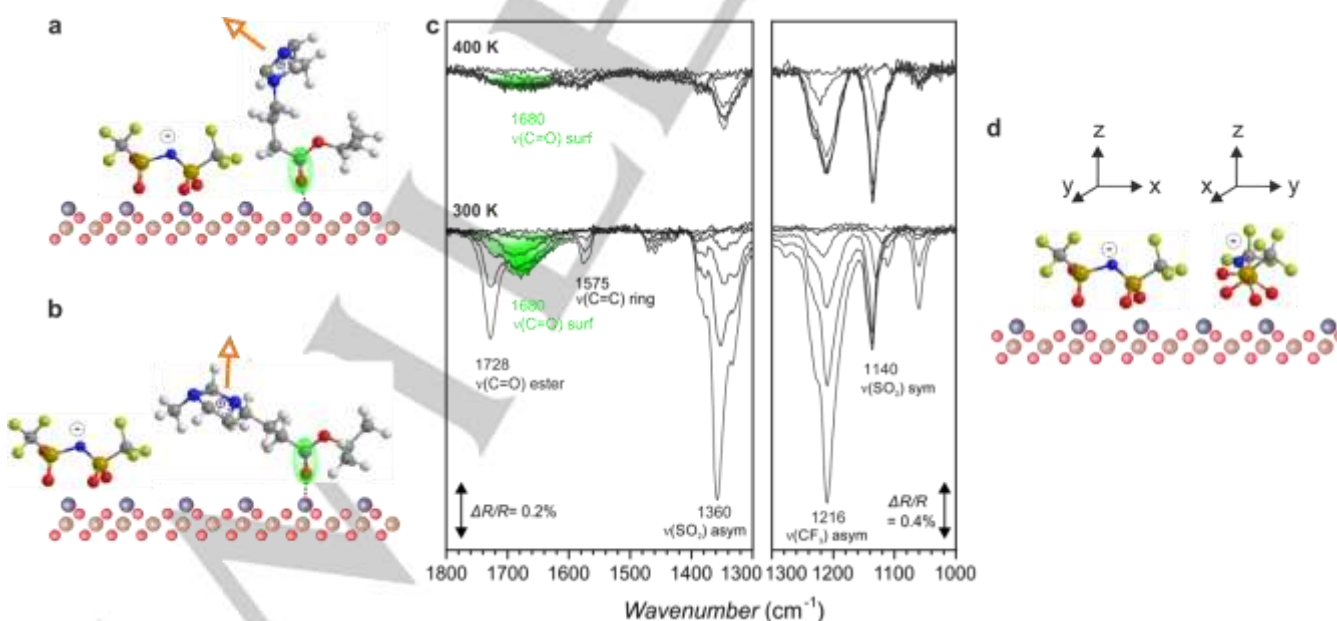
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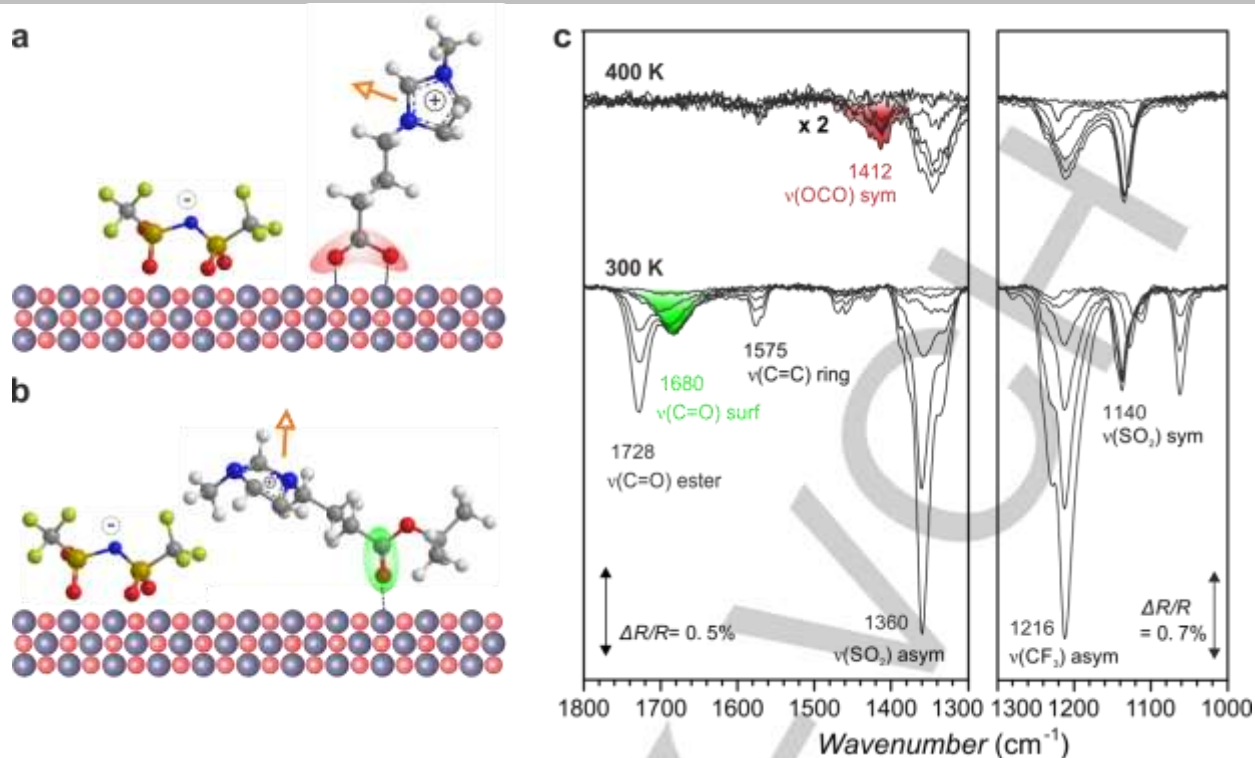
**Scheme 1** Molecular structure of 3-(4-isopropoxy-4-oxobutyl)-1-methylimidazolium bis(trifluoromethylsulfonyl)imide ([IPBMIM][NTf<sub>2</sub>]).



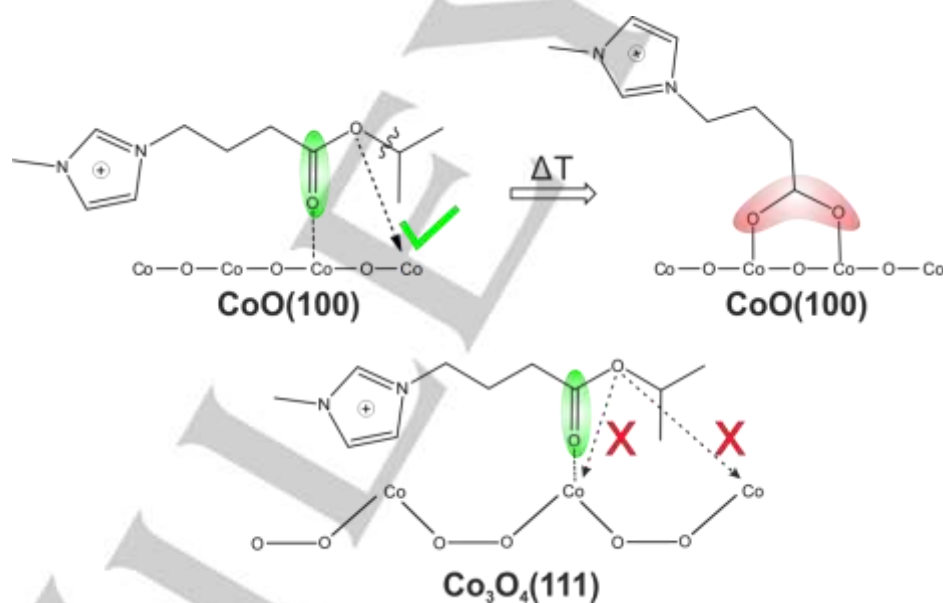
**Scheme 2** Atomic structure of the Co<sub>3</sub>O<sub>4</sub>(111) and CoO(100) surface. The Co<sub>3</sub>O<sub>4</sub>(111) surface is terminated by Co<sup>2+</sup> ions with a Co<sup>2+</sup>-Co<sup>2+</sup> distance of 5.7 Å. The CoO(100) surface is terminated both by Co<sup>2+</sup> and O<sup>2-</sup> ions with a Co<sup>2+</sup>-Co<sup>2+</sup> distance of 3.0 Å.



**Figure 1** Schematic representation of (a) [IPBMIM][NTf<sub>2</sub>] adsorbed on Co<sub>3</sub>O<sub>4</sub>(111) at 400 K and (b) [IPBMIM][NTf<sub>2</sub>] on Co<sub>3</sub>O<sub>4</sub>(111) at 300K; (c) In-situ IR spectra taken during adsorption of [IPBMIM][NTf<sub>2</sub>] on Co<sub>3</sub>O<sub>4</sub>(111); (d) schematic representation of the [NTf<sub>2</sub>]<sup>-</sup> anion adsorbed on Co<sub>3</sub>O<sub>4</sub>(111) with the SO<sub>2</sub> group oriented towards with the surface.



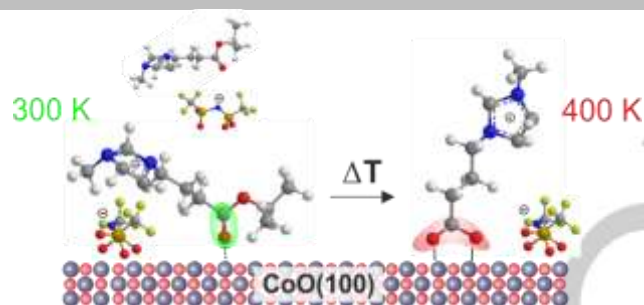
**Figure 2** Schematic representation of (a) [IPBMIM][NTf<sub>2</sub>] on CoO(100) at 400 K and (b) [IPBMIM][NTf<sub>2</sub>] on CoO(100) at 300K. (c) In-situ IR spectra taken during adsorption of [IPBMIM][NTf<sub>2</sub>] on CoO(100).



**Scheme 3** Interaction mechanism of [IPBMIM]<sup>+</sup> on Co<sub>3</sub>O<sub>4</sub>(111) and CoO(100). Only on CoO(100), the Co<sup>2+</sup>-Co<sup>2+</sup> distance allows forming a stable bridging carboxylate. On Co<sub>3</sub>O<sub>4</sub>(111), the large Co<sup>2+</sup>-Co<sup>2+</sup> distance prevents this adsorption geometry.

## COMMUNICATION

A functionalized imidazolium-based ionic liquid is covalently anchored to an oxide surface by deposition from the gas phase. In a highly structure sensitive reaction, the ionic liquid binds to the surface by thermally activated cleavage of an ester group and formation of a bridging carboxylate.



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